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ARTICLES

Determination of Cationic Surfactants in Soil Samples by the Disulphine Blue Active Substance (DBAS) Procedure[1]

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Abstract—A method for the determination of cationic surfactants in soil samples was developed and applied to a biodegradation study. Five different cationic surfactants (benzalkonium chloride, 1-dodecyl-3-methylimidazolium bromide, didecyldimethylammonium bromide, trihexyl(tetradecyl)phosphonium bromide and trihexyl(tetradecyl)phosphonium chloride) were selected for the study with the developed method upon extraction from soil samples with methanol. The samples were subjected to analysis as disulphine blue active substances using a visible spectrophotometer. The limits of detection for the proposed method ranged from 2 to 27 μg/g, which enabled the determination of cationic surfactants in soil samples. The results obtained in the biodegradation study were confirmed using liquid chromatography coupled with tandem mass spectrometry.

Keywords: cationic surfactant, solid sample, disulphine blue active substance, liquid chromatography, mass spectrometry

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Surfactants are compounds which consist of a polar head-group and a long hydrophobic tail-group. They tend to adsorb at the interface i.e. between two liquids (aqueous solution–organic solution) or between aqueous solution and air/soil. The hydrophilic part of the surfactant molecule is always directed towards the aqueous phase. Thereby, these compounds are accountable for the decrease of surface or interfacial tension. They play a number of fundamental roles in industry, mainly in cleaning and washing processes, but they are also used as emulsifiers, softeners, suspension stabilizers, catalysts or compounds for adjustment of flow resistance [1–3]. Surfactants can be classified into four different groups based on their form in aqueous solutions: anionic, cationic, zwitterionic and nonionic.

World production of surfactants is estimated at 12.7 mln tons per year, 75% of which are commodity anionic and nonionic surfactants. The total annual production of surfactants in Western Europe is 2 million tonnes (2013) [4]. Cationic surfactants are only a small part of this production, i.e. 229000 tonnes (2013) [4]. Cationic surfactants contain a positively charged hydrophilic part e.g. ammonium, phosphonium or sulfonium ion. This group has no wash activity effect, but fastens the molecules to the surfaces where they might provide softening, antistatic, soil repellent, anti-bacterial or corrosion inhibitory effects. Their most typical applications are softeners and antistatic agents. However, because of their strong biological activity, cationic surfactants are often applied as disinfectants in cleaning processes (including industrial and home usage) or as herbicides sprayed directly on crops. Their antifungal properties were also proven, and therefore they are widely used as wood protection agents [2, 3]. During emergency situations, such as serious outbreaks of avian influenza or foot and mouth disease, quaternary ammonium surfactants are also used as disinfectants sprayed on humans, buildings and the equipment [5–7].

Quaternary ammonium surfactants enter the environment and can bind to soil. Their leaching to water is possible but considerable amounts of these compounds can still be adsorbed on soil particles. Due to high biological activity, their biodegradation can be problematic, therefore, high concentrations of these compounds can be found in contaminated regions. Due to this reason, the determination of these compounds is an important task, as it enables studying contamination of different regions.

[1] The article is published in the original.

Reports regarding the development of new analytical methods for the determination of quaternary ammonium compounds in solid environmental samples are limited. There were studies on their determination in sediments [8–11] in which Soxhlet extraction, ultrasonic-assisted extraction, pressurized liquid extraction and supercritical fluid extraction were used for isolation of these compounds. The determination was conducted mainly with the use of liquid chromatography-mass spectrometry (**LC–MS**) [8–10]. More affordable UV-Vis and fluorescence detectors were used with HPLC in normal phase mode but their application required usage of post-column addition of ion-pairing reagent in water and subsequent on-line phase separation before measurement [11].

Although chromatographic methods are sensitive and give reliable results, the procedures used for the determination of cationic surfactants are sometimes tedious and complicated. Surfactants containing a number of different homologues are also problematic in quantification. Since it is not always required to collect information on different cationic surfactants present in samples, more affordable and simple spectrophotometric methods can be used. Good accuracy and precision as well as satisfactory sensitivity can be obtained using extraction-spectrophotometric disulphine blue active substance (**DBAS**) method. Other advantages of this method include short analysis time and low cost of chemicals used. The low price of a spectrophotometer is also worth mentioning. As a result, the extraction-spectrophotometric DBAS method found wide interest in the scientific community. However, its application to cationic surfactants was so far limited to water and aerosol matrices [2, 12–15].

The aim of this study was to develop a new analytical procedure based on the extraction-spectrophotometric DBAS method for the determination of cationic surfactants in soil samples. These compounds can be found in the environment due to a number of industrial processes as well as direct spraying during avian influenza. It was also demonstrated that the newly developed method can be competitive with an existing LC–MS method in terms of speed and low cost while maintaining satisfactory results.

EXPERIMENTAL

Chemicals and reagents. MS-grade methanol and ammonium acetate used as LC–MS mobile phase constituents were purchased from POCh (Gliwice, Poland) and Sigma-Aldrich (Poznań, Poland), respectively. High purity water was prepared by reverse osmosis in a Demiwa system from Watek (Ledec nad Sazavou, Czech Republic), followed by double distillation in a quartz apparatus. The remaining chemicals were of analytical grade and purchased from POCh. Cationic surfactants were synthesized in the Institute of Technology and Chemical Engineering at Poznan University of Technology according to previously published procedures [16, 17]. The list of the studied cationic surfactants is given in Table 1.

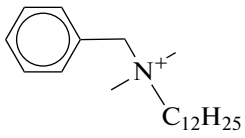
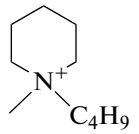
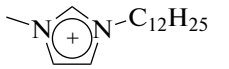
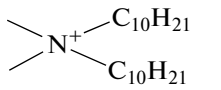
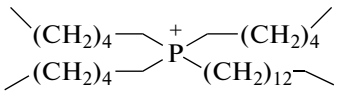
Sample collection and handling. Soil used in the experiments was collected from a city park in Poznan, Poland (N 52.4011445, E 16.9222993) and characterized as fine grained silt loam type OL belonging to organic silts and organic silty clays of low plasticity according to Unified Soil Classification System. The composition (%) of experimental soil was as follows: clay 4 ± 1, silt 83 ± 3, sand 13 ± 2. Detailed characteristics of the soil: organic carbon 5.4 ± 0.3 g/kg, nitrogen 0.57 ± 0.07 g/kg, phosphorous 0.080 ± 0.005 g/kg, pH 7.0 ± 0.7, bulk density 1.41 ± 0.06 ton/m^3, porosity 0.46 ± 0.03 m^3/m^3, moisture $18 \pm 1\%$, cation exchange capacity 22.1 ± 0.8 cmol$_c$/kg (standard deviations for 3 measurements are shown).

Extraction of cationic surfactants from soil and their determination using DBAS method. The collected soil was dried and grinded in a ball mill. For recovery studies, it was spiked with cationic surfactants at 4 mg/g. Extraction was carried out using 3 portions of methanol (6 mL each) per 1 g of sample. The samples were shaken with each portion of methanol using a mechanical shaker type 357 (ELPIN, Poland) at 200 cycles/min. The extracts were combined, filtered through 0.2 μm filter and diluted to 20 mL with methanol. An aliquot of this solution (not bigger than 3 mL) was added to a plastic container. Then, 15 mL of water, 2.5 mL of pH 5 acetic buffer, 1 mL of 0.064% disulphine blue solution and 10 mL of chloroform were added. The container was shaken for 20 min using a mechanical shaker. Absorbance of chloroform extract was read at 624 nm.

Extraction of cationic surfactants from soil and their determination using DBAS reference procedure. Sample treatment and LC–MS/MS analysis of cationic surfactants was done as described previously [18]. Briefly, approx. 0.4 g of the soil samples were subjected to ultrasound-assisted extraction with three 1-mL portions of methanol. The extracts were combined, filtered through a 0.2 μm PTFE syringe filter and diluted with a methanol–water (80 : 20, v/v) solution.

The chromatographic system UltiMate 3000 RSLC from Dionex (Sunnyvale, CA, USA) was used. Five-μL samples were injected into a C18 Hypersil GOLD column (100 × 2.1 mm, 1.9 μm) with a 2.1 mm I.D. filter cartridge (0.2 μm) from Thermo Scientific (Waltham, MA, USA). The mobile phase consisted of 5×10^{-3} M ammonium acetate in water and methanol at a flow rate of 0.2 mL/min at 35°C. Gradient elution was performed by linearly increasing the percentage of organic modifier from 85 to 100% in 4 min and maintained at 100% for 3 min. The LC column effluent was directed to the API 4000 QTRAP triple quadrupole mass spectrometer from AB Sciex (Foster City, CA,

Table 1. Description of studied cationic surfactants and analytical conditions used in their liquid chromatography-tandem mass spectrometry determination

Cationic surfactant	Abbreviation	Cation structure	Ionization source	MRM transitions, m/z	Collision energy, V
Benzalkonium chloride	BCl		ESI	304 → 212	29
1-Butyl-1-methylpiperidinium bromide	BMPBr		ESI	156 → 100	26
1-Dodecyl-3-methylimidazolium bromide	DMIBr		ESI	251 → 83	30
Didecyldimethylammonium bromide	DDDMABr		ESI	326 → 186	38
Trihexyl(tetradecyl)phosphonium bromide	THTDPBr		APCI	483 → 229	70
Trihexyl(tetradecyl)phosphonium chloride	THTDPCl				

Note: MRM—multiple reaction monitoring, ESI—electrospray ionization, APCI—atmospheric pressure chemical ionization.

USA) through the ESI source, which operated in positive ion mode for analyses of cations. The dwell time for each mass transition detected in the MS/MS multiple reaction monitoring mode was set to 200 ms. All the ions were detected using the following settings for the ion source and mass spectrometer: curtain gas 10 psi, nebulizer gas 40 psi, auxiliary gas 45 psi, temperature 400°C and collision gas medium. The declustering potential was 50 V. The detected mass transitions and specific parameters of each analyte were summarised in Table 1.

The analytical conditions were changed for the analysis of low polar trihexyl(tetradecyl)phosphonium cation. The same HPLC–MS/MS system was used but with the APCI source and different HPLC conditions. Five-μL samples were injected into a phenyl XBridge column (50 × 3.0 mm, 2.5 μm) from Waters (Milford, MA, USA). The mobile phase employed in the analysis consisted of 95% methanol at a flow rate of 0.6 mL/min at 40°C. The LC column effluent was directed to the APCI ionization source. The source operated in positive ion mode. The dwell time for the mass transition detected in the MS/MS multiple reaction monitoring mode was set to 100 ms. The following settings for the ion source and mass spectrometer were used: curtain gas 20 psi, ion source gas 50 psi, temperature 350°C, nebulizing current 3 μA, collision gas 6 psi and declustering potential 50 V. Further parameters were included in Table 1.

RESULTS AND DISCUSSION

Method development. The response of six selected cationic surfactants was tested using a series of standard solutions. The obtained calibration curves (Fig. 1) indicate a very low sensitivity of the DBAS procedure to 1-butyl-1-methylpiperidinium cation. This cation is more polar in comparison to other tested cations. Therefore, extraction of its blue complex with chloroform is diminished, resulting in a response similar to the blank solution. As a result, 1-butyl-1-methylpiperidinium cation was excluded from further studies.

Calibration curves for the other tested compounds indicate a higher sensitivity of the DBAS method, as the slopes of calibration lines are much higher than for 1-butyl-1-methylpiperidinium cation. Although the slopes differ slightly for different cations, they are almost identical for cationic surfactants containing the same cation and different anions, i.e. for trihexyl(tetradecyl)phosphonium bromide and trihexyl(tetradecyl)phosphonium chloride. The obtained curves are linear up to 70 or 100 μg of surfactant added to the extraction system with R^2 not less than 0.99.

Since the procedure requires extraction of the surfactant blue complex from the water–methanol solution to chloroform, it is of great importance to test the influence of methanol on the obtained results. Therefore, different volumes of methanol were added to the buffered disulphine blue solution to test the possible

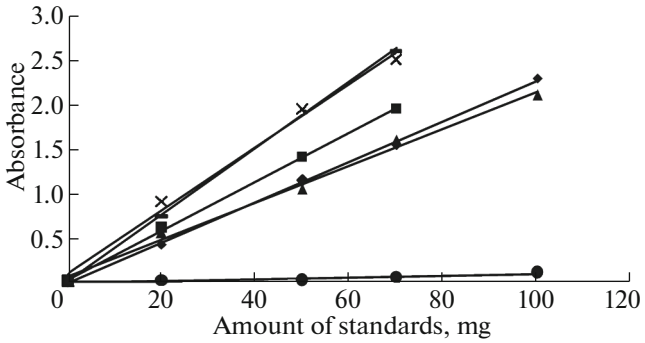


Fig. 1. Calibration curves obtained for studied cationic surfactants. (◆) THTDPBr, (●) BMPBr, (▬) BCl, (■) DDDMABr, (▲) THTDPCl, (×) DMIBr.

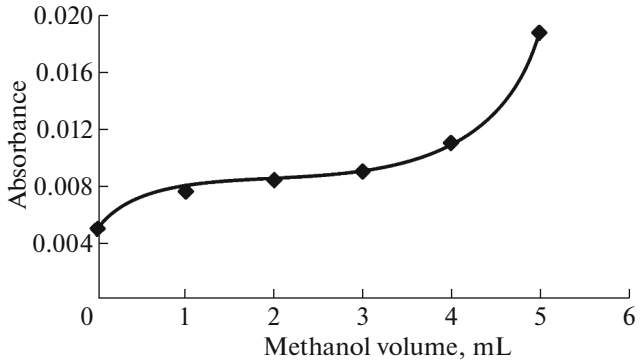


Fig. 2. Influence of methanol volume on absorbance.

increase of absorbance. As it is presented in Fig. 2, addition of up to 3 mL of methanol had little influence on the obtained results as the absorbance was at a very low level. Increase of methanol volume to 4 and further 5 mL considerably changed the absorbance. Thus, 3 mL was selected as maximum methanol volume in the final procedure.

Limits of detection (**LOD**) and quantitation (**LOQ**) of the DBAS procedure were tested using the response of the blank solution. LOD was assessed as concentration calculated for blank solution plus three standard deviation (**SD**) values (LOD = conc + 3SD), and LOQ was expressed as concentration calculated for blank solution plus six standard deviation values (LOQ = conc + 6SD). Seven blank samples were measured and apparent concentration of each cationic surfactant was calculated using appropriate calibration curve. Average concentrations and SD values were calculated which allowed to assess LOD and LOQ values presented in Table 2.

The developed analytical procedure was combined with extraction of cationic surfactants from the soil matrix. Since methanol was used in preparation of standards and it was also shown that it had little influence at DBAS procedure, this solvent was used for the extraction of cationic surfactants from soil samples. Triple extraction of blank soil samples showed no interference. Three methanolic extracts were combined and then the cationic surfactants were re-extracted to chloroform as disulphine blue complexes. The results presented in Table 3 show recovery ranging from 60 to 90%. Higher results were observed for the phosphonium than for the ammonium surfactants. Precision of the developed method was determined using trihexyl(tetradecyl)phosphonium cation. Five spiked soil samples were tested and the precision expressed as RSD equal to 1.7% was obtained. After the methanol volume was set to 3 mL and recoveries were assessed, the LOD and LOQ values were recalculated for the developed method (Table 3).

Table 2. Limits of detection and quantitation for the studied cationic surfactants

Cationic surfactant	LOD, μg	LOQ, μg
Trihexyl(tetradecyl)phosphonium bromide	0.5	0.77
Trihexyl(tetradecyl)phosphonium chloride	2.9	3.1
Didecyldimethylammonium bromide	1.3	1.5
Benzalkonium chloride	0.15	0.27
1-Dodecyl-3-methylimidazolium bromide	2.6	2.8

Application of the method in biodegradation studies. The DBAS method was used to assess the biodegradation of the selected cationic surfactants in soil. The soil samples were spiked with 500 mg of cationic surfactant per 100 g of dry soil. After 2 years, the content of cationic surfactants was determined using DBAS method and a reference LC–MS/MS method. Results presented in Table 4 show a good correlation between the values obtained by both methods. The DBAS results were used to calculate the biodegradation of cationic surfactants in the soil samples. Results presented in Table 5 show biodegradation exceeding 90% for most of tested cationic surfactants. However, the biodegradation of trihexyl(tetradecyl)phosphonium chloride was only at 28%. This can be surprising as the biodegradation of the same cation in the presence of bromide instead of chloride anion is very high. The reason of this different behaviour is unknown, although it could be assumed that it was connected with biodiversity of microorganisms in the soil. As it was found in our previous experiments (results not included), biodegradation of different compounds in the presence of selected strains is always comparable in repeated experiments but biodegradation with the use of sewage sludge sometimes differs considerably between repeated experiments.

CONCLUSIONS

New cationic surfactants are still synthesized and their influence on the environment is often unknown.

Table 3. Recovery, limits of detection and quantitation for cationic surfactants from soil

Cationic surfactant	Recovery, %	LOD, μg/g	LOQ, μg/g
Trihexyl(tetradecyl)phosphonium bromide	89.1	4	6
Trihexyl(tetradecyl)phosphonium chloride	87.5	22	24
Didecyldimethylammonium bromide	68.7	13	15
Benzalkonium chloride	59.8	2	3
1-Dodecyl-3-methylimidazolium bromide	65.5	27	28

Table 4. Content (mg/g dry mass) of cationic surfactants in soil samples determined by using DBAS and reference LC–MS/MS methods

Cationic surfactant	DBAS	LC–MS/MS
Trihexyl(tetradecyl)phosphonium bromide	0.26 ± 0.01	0.14 ± 0.04
Trihexyl(tetradecyl)phosphonium chloride	3.60 ± 0.07	4 ± 1
Didecyldimethylammonium bromide	<LOD	0.07 ± 0.04
Benzalkonium chloride	0.030 ± 0.001	0.017 ± 0.006
1-Dodecyl-3-methylimidazolium bromide	<LOQ	0.013 ± 0.007

Table 5. Biodegradation of cationic surfactants in soil during 2 years, as determined using DBAS method

Cationic surfactants	Biodegradation, %
Trihexyl(tetradecyl)phosphonium bromide	94.8
Trihexyl(tetradecyl)phosphonium chloride	28.0
Didecyldimethylammonium bromide	100.0
Benzalkonium chloride	99.4
1-Dodecyl-3-methylimidazolium bromide	100.0

Their monitoring is important as some of them can be persistent, especially in soil. Some instrumental techniques used for their determination, including LC–MS/MS, are expensive and require qualified analysts which limits their usage. The presented spectrophotometric method, based on the determination of disulphate blue complex, is a fast and low-cost alternative. It can be easily used for monitoring of cationic surfactants in environmental samples and for their determination in biodegradation tests.

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